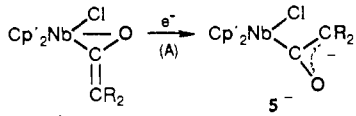
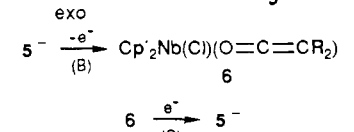
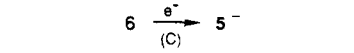


(3)



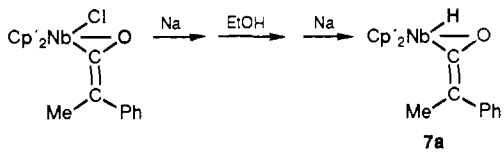
(4)



(5)

(Figure 1, first sweep) represents reduction and isomerization to endo metallaenolate (5^-), wave B represents oxidation of this to a ketene complex (**6**) which is an isomer of the starting material, and that wave C in the second sweep represents reduction of **6**. Possible formulations for **6** include *endo*-C=O or -C=C bound ketene complexes; this point is under study. The relative heights of waves A and C in the second sweep depend on ketene substituents and scan rate, suggesting that this ligand is involved in the isomerization process. We have also noted that added chloride (as LiCl) has no effect on the voltammetry, and that standardization with $Cp_2Fe^{0/+}$ indicates that the processes depicted in Figure 1 are one-electron events. The key observation, then, is that the ketene complexes undergo a one-electron reduction via a process which involves a structural change in the ketene ligand.

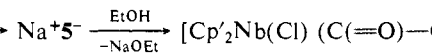
In an attempt to generate and trap a niobaenolate, **3** was treated with sodium amalgam (in ether) and quenched with added ethanol. Further investigation revealed that the one-pot process requires 2 equiv of reductant and that the proton source must be added in the presence of the second reducing equivalent. The resulting product is *exo*-(*E*)-$Cp'_2Nb(H)$ (OCCMePh) (**7a**, eq 6), isolated



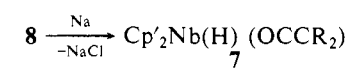
(6)

7a

as an off-white solid in 60% yield; in solution it undergoes slow equilibration to a 50:50 mixture of **7a** and *exo*-(*Z*)-**7b** (these assignments are corroborated by NOE experiments). These are the first metal complexes to contain both hydride and ketene ligands. We propose that the synthetic sequence involves reduction to a metallaenolate (as indicated by the voltammetric experiments, eq 3), which is protonated at carbon to give **8**.[9] This Nb(IV)



(7)



(8)

acyl is rapidly reduced by the second equivalent of sodium, with loss of Cl^-. The resulting Nb(III) acyl then undergoes β-H elimination to give the ultimate product. Although Baird has observed acyl β-H elimination resulting in metal hydride and free ketene,[10,11] there is no example of such a process giving a ketene hydride complex. Consistent with the proposed mechanism, we note that (a) if niobaenolate 5^- is deliberately oxidized prior to addition of the proton source, **3** is regenerated; (b) if the initially formed intermediate 5^- is removed from the excess amalgam before it is treated with the proton source, a mixture of **3** and **7** results; and (c) the use of MeOD as quencher results in D incorporation only at the Nb-D site. These observations would seem to preclude alternate mechanisms involving loss of chloride in the first reduction step or an initial two-electron reduction (also, a reduced niobium center should react with ethanol to give H_2 and Nb-OEt; neither is observed).

Lastly, we note that the synthetic sequence of e^-, H^+, e^- is equivalent to treatment with hydride. However, treatment of **3** with $LiAlH_4$ gave rapid conversion to $Cp'_2Nb(\mu\text{-}H)_2AlH_2$, while milder hydride sources (MBH_4) failed to react. Similarly, treatment of $Cp'_2Nb(BH_4)$ or $Cp'_2Nb(H)$ (PPh_3) with ketenes gave intractable products, suggesting niobium-hydride-induced ketene polymerization.[12] Thus, a ketene-mediated synthesis of **7** appears to be the only viable route, and it illustrates the fact that the complexed ketene can support chemistry with which free ketenes are incompatible. Further studies of the utility of the complexed ketenes are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corp. for support and Gayle Schulte for performing the crystallographic study.

Supplementary Material Available: Spectral data (^1H NMR and IR) for **1-4** and **7** (3 pages). Ordering information is given on any current masthead page.

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Oxygen-Atom Transfer from Nitrous Oxide. Identification of Intermediates in the Oxidation of Diphenylacetylene at Group 4 Metal Centers and the Structural Characterization of $(\eta\text{-}C_5Me_5)_2Ti\{N(O)NCPh{=}CPh\}\cdot{}^1/_2C_7H_8$

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Nitrous oxide is a thermodynamically potent oxidant for oxo-transfer reactions (ΔG_f° = 25 kcal/mol), but it is remarkably kinetically inert in the absence of a suitable activating center (usually a transition metal);[1,2] moreover, the sole byproduct of oxo transfer from N_2O, dinitrogen, is an innocent, unreactive one. For these reasons nitrous oxide is an attractive oxygen-atom source for effecting selective chemical oxidations. Other workers, most notably Bottomley's group, have exploited N_2O as a reagent for preparing unusual transition-metal-oxo clusters,[3,4] while Lunsford

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has shown it to be a good oxo donor in selective methane oxidation on silica/molybdate catalysts.[5] We have been studying reactions of group 4 transition-metal complexes with N_2O that result in oxidation of a coordinated ligand instead of formation of metal-oxo species. In this regard we have uncovered interesting transformations, like the oxidation of a metal hydride to hydroxide,[6] a metal phenyl to phenoxide,[6] and a coordinated cyclohexyne to an oxametallacyclobutene derivative.[7] Herein we report the results of the reactions of N_2O with the diphenylacetylene complexes of permethyltitanocene and -zirconocene, $Cp^*_2M(C_2Ph_2)$ ($Cp^* = \eta$-C_5Me_5; **1**, M = Ti; **2**, M = Zr).[8]

Nitrous oxide (1 equiv, 20 °C) reacts with toluene solutions of **1** or **2** to afford ~70% yields of the products of N_2O insertion into a M–C(alkyne) bond, $Cp^*_2M\{N(O)NCPh{=}CPh\}$ (**3**, M = Ti; **4**, M = Zr) (eq 1).[9] The characterization of these N_2O adducts follows from standard spectroscopic (^1H, ^{13}C NMR, and IR) and analytical data as well as from a single-crystal X-ray diffraction study of **3**.[10] The ^1H NMR spectrum (C_6D_6) of **3** exhibits a singlet at δ 1.76 for the methyl protons of the Cp* rings and multiplets at δ 6.30–7.82 for two inequivalent phenyl groups. The appearance of a doublet (δ 141.5; $|^1J_{^{15}NC}| = 9$ Hz) in the ^{13}C NMR spectrum of [^{15}N]-**3** (prepared from $^{15}N{=}N{=}O$) provides clear evidence that the terminal N-atom of nitrous oxide has been covalently attached to one of the nonaryl carbons of the C_2Ph_2 ligand (the resonance is a singlet in **3**).[11] Comparison of the infrared spectra of **3** and [^{15}N]-**3** allows for the probable identification of ν_{NN} as a strong band at 1339 cm^{-1} (1335 cm^{-1} in [^{15}N]-**3**); four weak bands also shifted (from 1181, 1173, 1067, and 923 cm^{-1} in **3**) to lower energy by ~4-5 cm^{-1} in [^{15}N]-**3**. **4** is spectroscopically similar to **3**,[9] exhibiting ^1H NMR resonances (C_6D_6) at δ 1.77 (s, 30 H) and 6.83–7.84 (m, 10 H). The ^{13}C NMR spectrum of [^{15}N]-**4** (prepared from **2** and $^{15}N{=}N{=}O$) also shows a doublet resonance with characteristic $^1J_{^{15}NC}$ coupling (δ 138.5; $|^1J_{^{15}NC}| = 7$ Hz).[11]

Reactions between N_2O and metal complexes in which N_2 is not extruded are rare. Nitrous oxide forms a coordination complex in $[Ru(N_2O)(NH_3)_5^{2+}]$, but the weak ligation of N_2O has prevented its characterization by X-ray structural methods.[12,13] A thermally unstable intermediate (that does not lose N_2 at −78 °C) has been observed in the reaction of N_2O with Cp_2V that yields $Cp_5V_5(\mu_3\text{-}O)_6$.[4g] Because of the unprecedented stabilities of **3** and **4** with respect to N_2 loss, we carried out a structural study of **3** by X-ray diffraction methods to ascertain the binding mode of N_2O in these compounds. A perspective view of the structure of **3** with selected bond angles and distances is shown in Figure 1. In view of the oxophilic character of d^0, group 4 metal centers, it is somewhat surprising that the oxygen atom of **3** is not bound to Ti, but this is consistent with calculations that suggest that interactions of metal complexes with N_2O should occur preferentially via the terminal nitrogen atom.[14] The metrical parameters of **3** are most consistent with a planar five-membered metallacycle containing approximately localized C–C and N–N double bonds. This unusual metallacycle is thus best described as an *azoxy* derivative, with the heteroatomic bond distances in **3** being comparable to the corresponding distances found in *p*-azoxyanisole, *p*-$MeOC_6H_4{-}N(O){=}N{-}C_6H_4$-*p*-OMe, where N–O = 1.279 (4) Å and N–N = 1.218 (5) Å.[15]

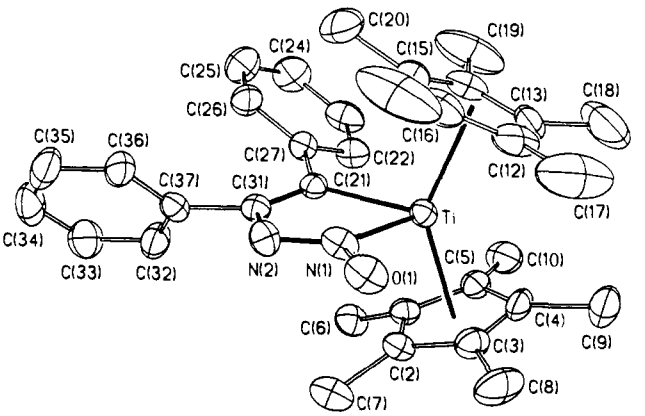

Figure 1. Molecular structure of $(\eta\text{-}C_5Me_5)_2Ti\{N(O)NCPh{=}CPh\}$ (**3**). Ti–CNT(1–5), 2.119 (6); Ti–CNT(11–15), 2.114 (6); Ti–N(1), 2.088 (4); Ti–C(21), 2.210 (5); N(1)–N(2), 1.294 (7); N(1)–O(1), 1.281 (6); N(2)–C(31), 1.435 (7); C(21)–C(31), 1.344 (7) Å. CNT–Ti–CNT, 141.4 (2); N(1)–Ti–C(21), 73.8 (2); Ti–N(1)–N(2), 124.3 (3); Ti–N(1)–O(1), 116.3 (3); O(1)–N(1)–N(2), 119.3 (4); N(1)–N(2)–C(31), 108.8 (4); N(2)–C(31)–C(21), 122.7 (5); Ti–C(21)–C(31), 110.1 (4)°.

At ambient temperature (even in the solid state), **4** is thermally unstable with respect to loss of N_2 (0.96 equiv/Zr) and formation of a red oxametallacyclobutene complex $Cp^*_2Zr(OCPh{=}CPh)$ (**5**) in 85% isolated yield (eq 2). **3** is more stable to N_2 loss, decomposing only at ~50 °C to several products. **5** has been characterized by standard spectroscopic (^1H, ^{13}C NMR, and IR) and analytical techniques[9] and by its protonolysis with HCl (yielding $Cp^*_2ZrCl_2$ and deoxybenzoin, $PhCH_2C(O)Ph$) demonstrating that the oxygen atom has been added to the alkyne (eq 2).[16] The ^1H NMR spectrum (C_6D_6) of **5** exhibits a singlet at δ 1.81 for the methyl protons of the Cp* rings and multiplets at δ 6.90–7.99 for two inequivalent phenyl groups. Kinetic measurements (^1H NMR, 30 °C → 60 °C) show the decomposition of **4** to have a first-order dependence on [**4**], with $\Delta H^{\ddagger} = 19.3 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -10.1 \pm 1$ eu.[17] The negative entropy

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(10) Crystallographic data for $3{\cdot}^1/_2C_7H_8$: $C_{34}H_{40}N_2OTi{\cdot}^1/_2C_7H_8$, monoclinic, $P2_1/n$, $a = 15.100$ (5) Å, $b = 17.893$ (6) Å, $c = 11.988$ (2) Å, $\beta = 90.29$ (2)°, $V = 3239$ (1) Å^3, $Z = 4$, μ (MoKα) = 2.99 cm^{-1}, $T = 293$ K, D(calcd) = 1.203 g·cm^{-3}, obsd rflxns (3σ) = 2650 for $4° \le 2\theta \le 45°$, R(F) = 6.54%, R(wF) = 6.73%, GOF = 1.334, $\Delta(\rho) = 0.48$ e·Å^{-3}, $N_o/N_v = 7.3$.

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(16) $PhCH_2C(O)Ph$ was identified by comparison to an authentic sample. See Supplementary Material for experimental details.

of activation suggests that N_2 loss from **4** to give **5** is not a concerted process and probably involves a rate-determining ligand rearrangement (perhaps ring expansion with formation of a Zr–O bond) before N_2 extrusion occurs. **5** is reactive toward a number of other small molecules, and elaboration of this reaction chemistry will be the topic of a future publication.

Acknowledgment. Financial support from the National Science Foundation (CHE-8818607) and an Alfred P. Sloan Foundation Research Fellowship (1989–1991) is sincerely appreciated by G.L.H. A summer fellowship under the N.S.F. Research Experiences for Undergraduates Program (NSF 8713014) is gratefully acknowledged by C.D.S. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant (NIH-CA-14599).

Supplementary Material Available: Experimental, spectroscopic (^1H, ^{13}C NMR, and IR), analytical, and crystallographic details and tables of atomic coordinates, bond angles and distances, anisotropic thermal parameters, and hydrogen atom coordinates (11 pages); table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

(17) Kinetic data were obtained on **4** prepared in situ from **2** and N_2O and reflect the rate of the disappearance of **4**, which was independent of $[N_2O]$. See Supplementary Material for experimental details.

Practical Enantioselective Diels–Alder and Aldol Reactions Using a New Chiral Controller System

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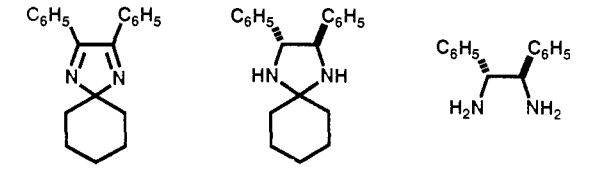
The Diels–Alder and aldol reactions are among the most useful of all synthetic processes for the construction of complex molecules, and, for this reason, they have been very extensively studied and refined. The development of enantioselective versions of these reactions, especially, has been the object of recent research in many laboratories.[1,2] Nonetheless, existing methodology is still not ideal, since there are drawbacks and limitations for all of the known procedures. Described herein is a new chiral controller system which has excellent practical potential because of the ready availability and recoverability of the chiral controllers and the high enantioselectivities which can be realized with predictable absolute configuration.

(±)-1,2-Diamino-1,2-diphenylethane (stilbenediamine, stien) has been prepared previously in six steps from ammonia and benzaldehyde[3] and efficiently resolved with tartaric acid to give both *R,R*-stein and *S,S*-stien,[3] the key ingredients of the controllers described herein. Although multigram amounts of stien can be prepared in this way, a much shorter synthesis has now been developed which provides this diamine economically and quickly on any scale. Reaction of benzil and cyclohexanone (1 equiv of each) with ammonium acetate–acetic acid at 120 °C for 1 h resulted in formation of cyclic bis-imine **1**[4] (97% yield), mp 105–106 °C, which was reduced stereospecifically with 4 equiv of lithium in 4:5 THF–liquid ammonia (0.3 M in **1**) at −78 °C for 2 h with addition of 2 equiv of ethanol in four portions to give the *trans*-imidazolidine **2** (95%). Treatment of a solution of **2** in methylene chloride successively with 2 N hydrochloric acid and aqueous base provided after removal of solvent (±)-stien (**3**), mp 81–82 °C, in 92% overall yield from **1**. After resolution[3] (tartaric acid) both the *R,R*- and *S,S*-forms of **3** (>99% optical purity) were converted to the crystalline bis-sulfonamides **4**, **5**, and **6**. Reaction of **4** in 1,2-dichloroethane at 80 °C with diisobutylaluminum hydride or trimethylaluminum (in toluene) afforded the corresponding cyclic amido aluminum alkyl, **7** or **8**. These reagents function effectively as chiral Lewis acids to catalyze a number of useful enantioselective Diels–Alder reactions.



1 **2** **3**

4 R=CF_3 **7** R=*i*-Bu **16** Ar=*p*-CH_3-C_6H_4

5 R=*p*-CH_3-C_6H_4 **8** R=CH_3 **17** Ar=*p*-NO_2-C_6H_4

6 R=*p*-NO_2-C_6H_4

The first reported highly enantioselective Diels–Alder reaction with an acrylate ester involved the 8-phenylmenthol ester (ca. 95% ee with cyclopentadiene and $AlCl_3$ catalysis)[5] which was far superior to the menthyl ester (ca. 40% ee with cyclopentadiene and $SnCl_4$ catalysis).[6] Nonetheless, when (*R,R*)-**7** (0.5 equiv) was employed as catalyst in the reaction of the acrylate ester of (−)-menthol with cyclopentadiene, an 85% yield of the endo-Diels–Alder adduct **9** with de of 97% was obtained after a reaction time of 24 h at −78 °C.[7] The absolute stereochemistry and high stereoselectivity of this reaction can be easily understood in terms of the most favorable transition-state geometry represented by **10**. As expected on this basis, the corresponding reaction of (*S,S*)-**7**, cyclopentadiene, and the acrylate ester of (−)-menthol is less selective (de of 52%),[8] as is the analogous reaction with methyl acrylate (ca. 50% ee). 3-Acrylyl-1,3-oxazolidin-2-one (**11**)[1g] was found to be a much more satisfactory reactant than simple acrylate esters. Thus, reaction of **11** and cyclopentadiene

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(7) The absolute configuration and de of the major product were determined by $LiAlH_4$ reduction, esterification of the resulting primary alcohol with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid chloride (MTPA-Cl), and ^1H NMR analysis at 500 MHz using reference standards.

(8) In addition, the use of (*R,R*)-**8** as catalyst in place of (*R,R*)-**7** afforded **9** with somewhat lower de (85%).

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